CNT-based Thermal Interface Materials for Load-Bearing Aerospace Applications

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2012 AFOSR Annual Grantees’/Contractors Meeting for M^4 Program
Arlington, VA

July 30th – Aug 3rd, 2012

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **AUG 2012**	2. REPORT TYPE	3. DATES COVERED **00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE **CNT-based Thermal Interface Materials for Load-Bearing Aerospace Applications**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Case Western Reserve University,Department of Mechanical and Aerospace Engineering,Cleveland,OH,44106**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the 2nd Multifunctional Materials for Defense Workshop in conjunction with the 2012 Annual Grantees’/Contractors’ Meeting for AFOSR Program on Mechanics of Multifunctional Materials & Microsystems Held 30 July - 3 August 2012 in Arlington, VA. Sponsored by AFRL, AFOSR, ARO, NRL, ONR, and ARL. U.S. Government or Federal Rights License

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**28**	

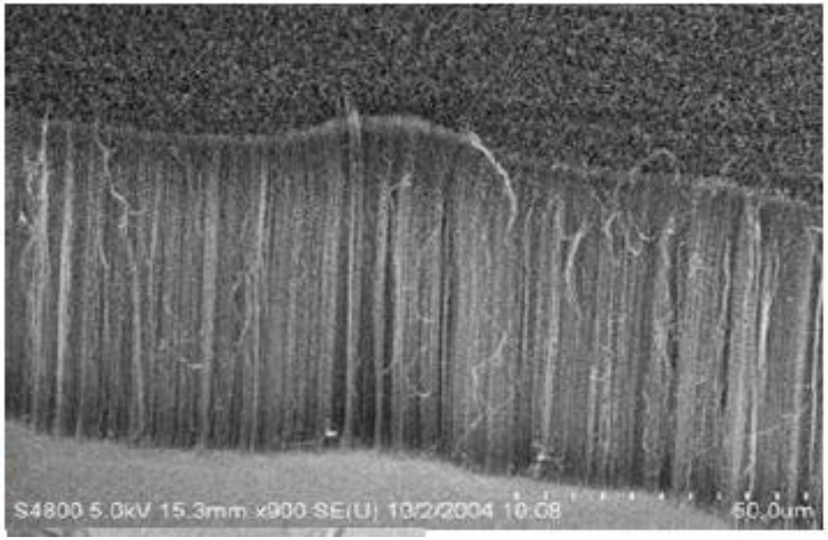
Objective

Develop multifunctional CNT-epoxy Thermal Interface Materials (TIMs) for load bearing aerospace applications.

Emphasis -

To increase thermal transport across a thermal interface by utilizing an array of Vertically Aligned MWCNTs.

Target k – 5 -7 W/(m-K)



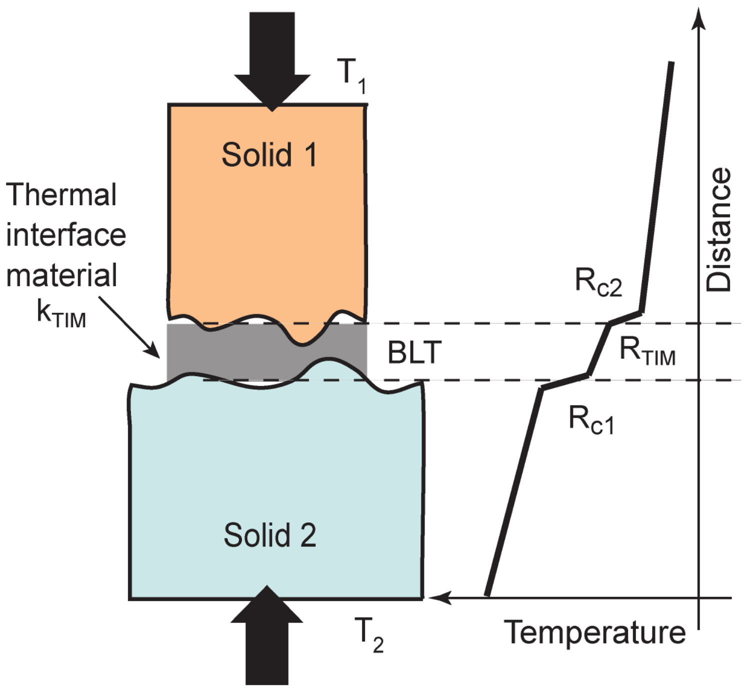
SEM picture of an array of vertically aligned carbon nanotube array grown on a silicon substrate.

Typical Thermal Interface

Total Thermal Interfacial Resistance

$$R_{\text{interface}} = R_{c1} + \frac{BLT}{k_{\text{TIM}}} + R_{c2}$$

BLT – boundary layer thickness



Minimize $R_{\text{interface}}$

$k_{\text{TIM}} \uparrow$

-- Use high thermal conductivity fillers

-- Minimize number of thermal interfaces

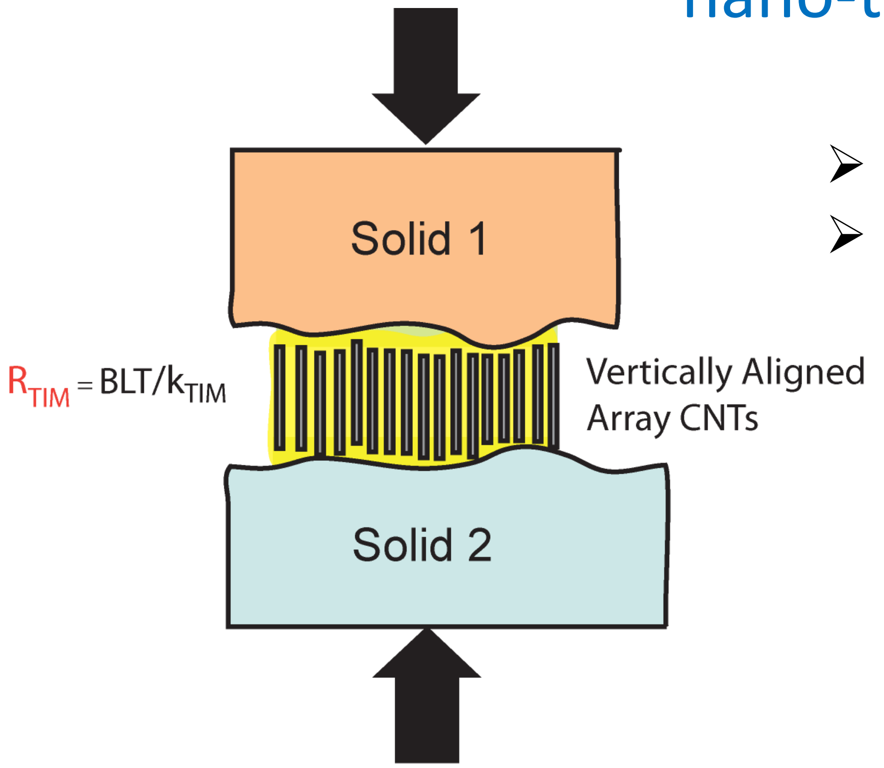
$R_c \downarrow$

-- Reduce air gaps – use smooth contacting surfaces

-- employ low melt-point materials (e.g. Sn), as capping layers

-- materials with compatible phonon spectra

Approach



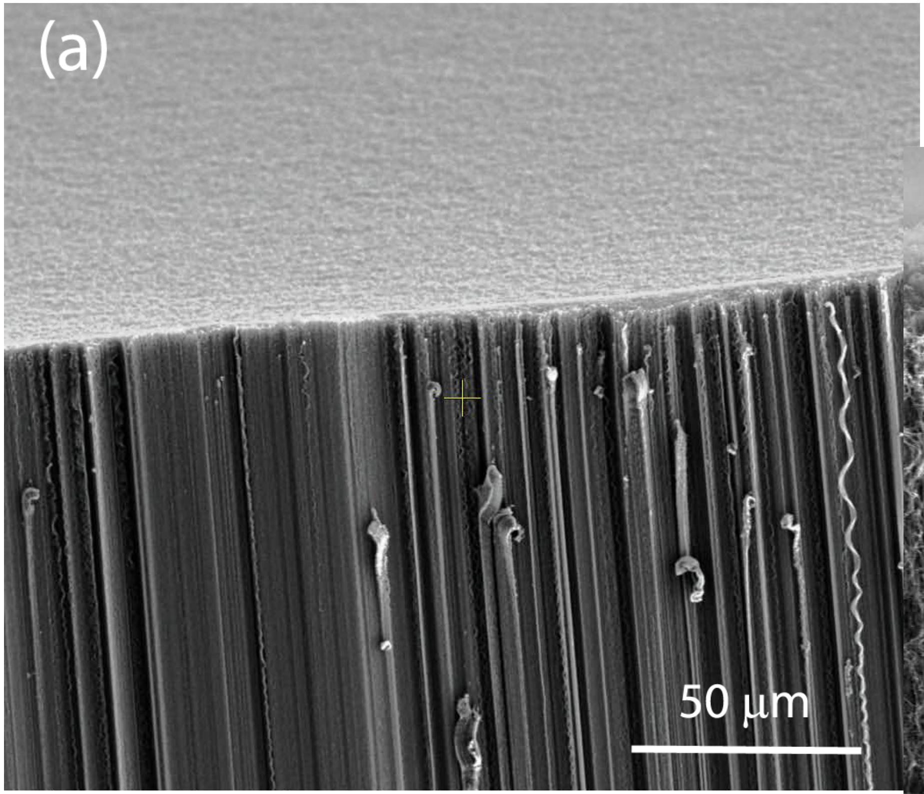
Vertically-aligned multi-wall Carbon nano-tubes in an epoxy matrix

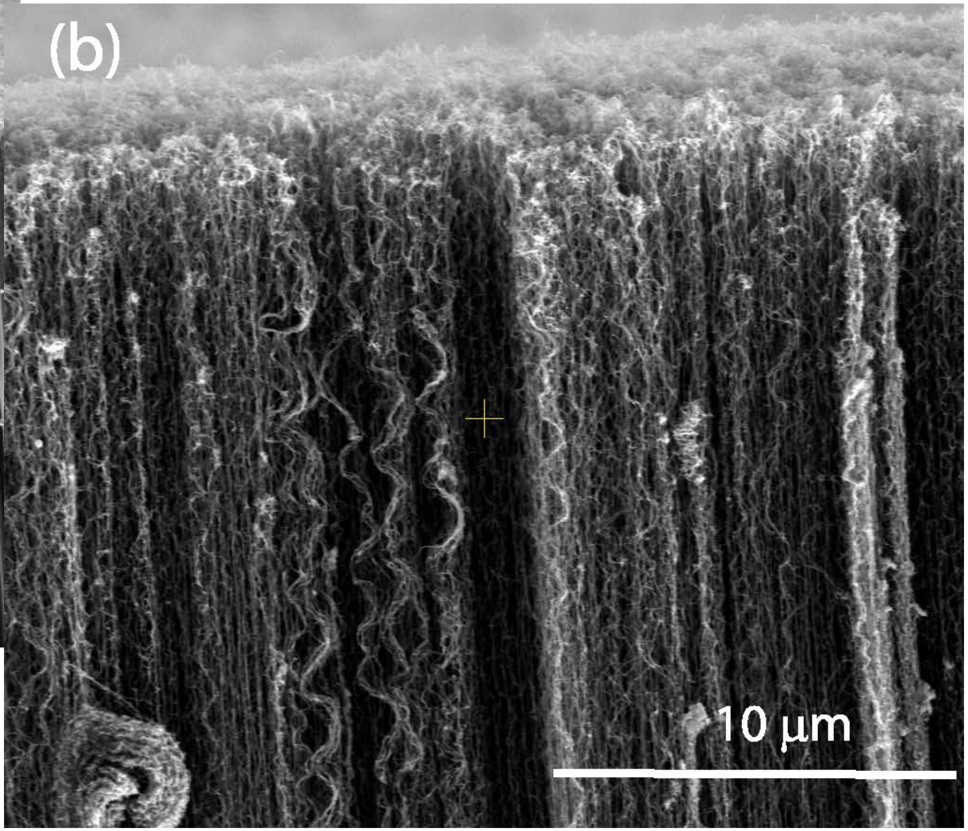
- k_{CNT}~ 100 W/m-K
- Use Sn capping metal layer to minimize phonon scattering at CNT-epoxy ends.

Assume 10% vol. fraction of VACNT in an epoxy matrix
(k_{epoxy} ~ 0.25W/m-K; k_{CNT}~ 100 W/m-K)

k_{TIM}~ 10 W/m-K

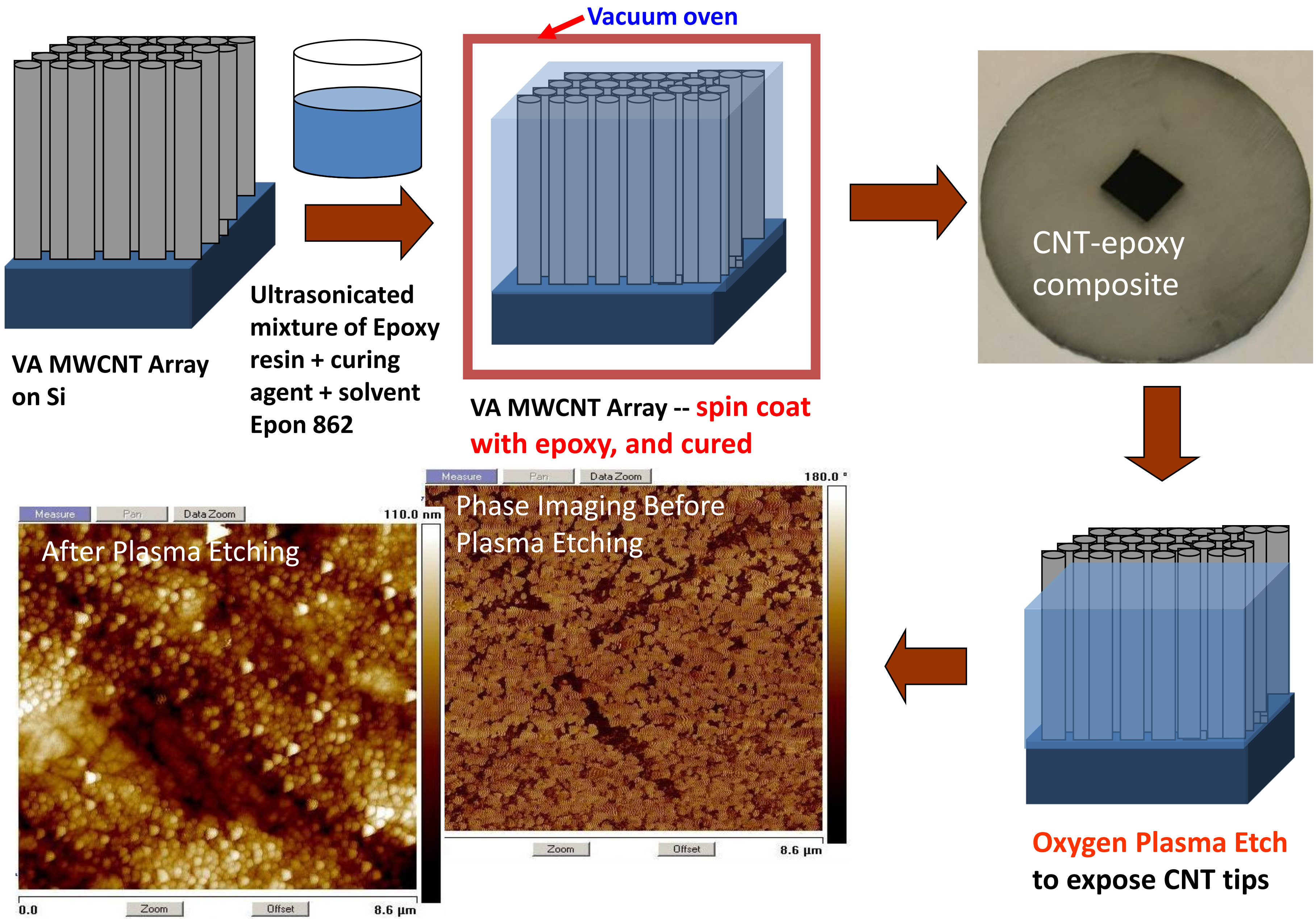
VA Multi-walled CNT Array



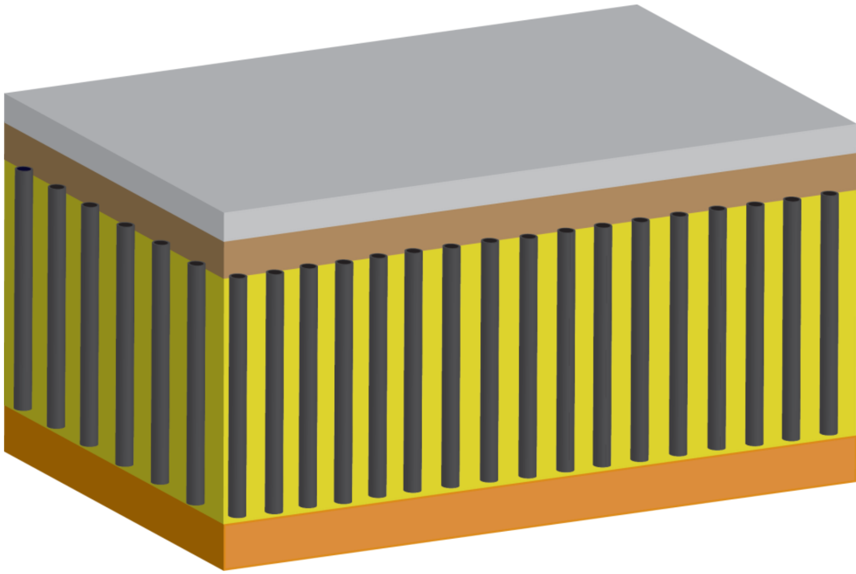


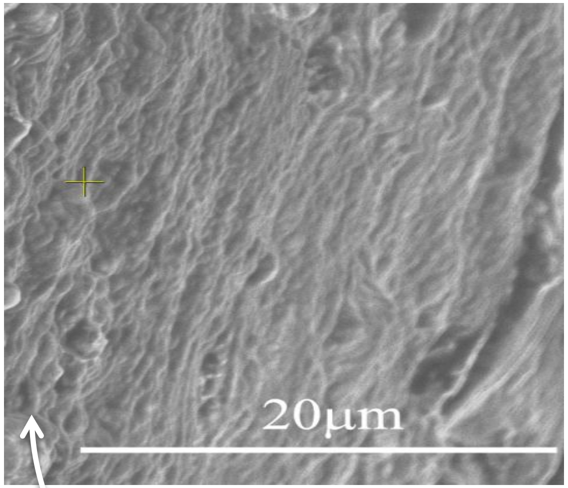
VA MWCNT array of MWCNTs ~ 1-2 mm in length grown by a thermal CVD process (pyrolysis of iron (II) phthalocyanine (FePc) under Ar/H_2 at 900 ^{0}C on a silicon wafer). Nanotube dia. 15 to 40nm.

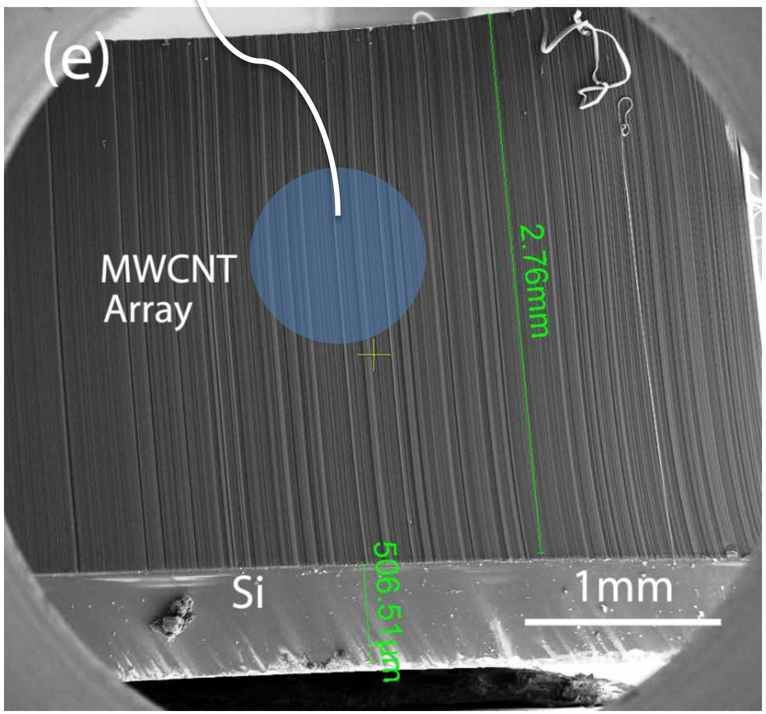
Fabrication of VACNT- epoxy Composite TIM



Vertically Aligned MWCNT-epoxy Composite







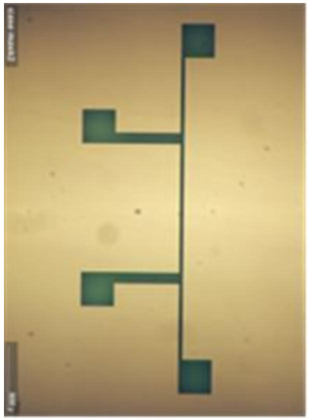
Tasks: **Characterize Thermal Transport across MWCNT-epoxy TIM**

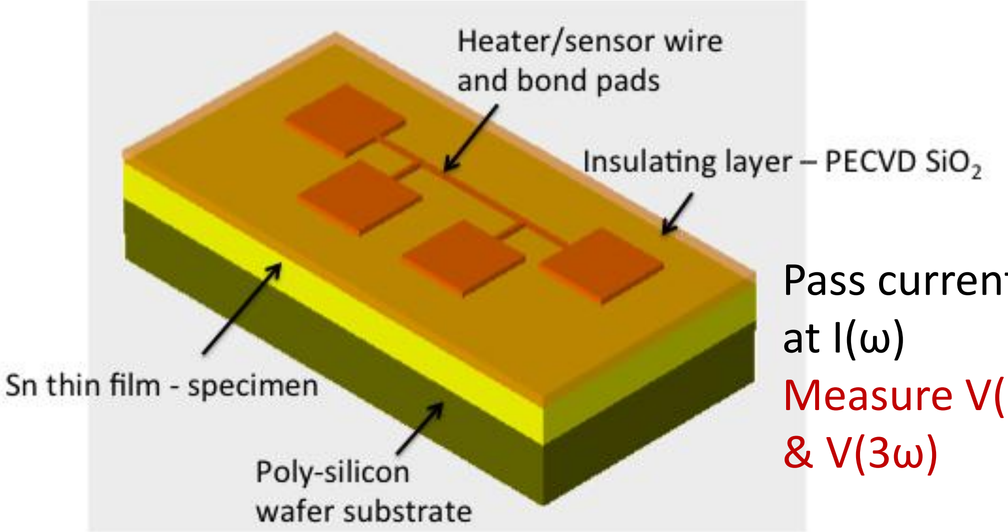
Individual components

- Individual MWCNTs; epoxy matrix;
- Sn capping layer
- Interfacial thermal resistance at the MWCNT ends & capping Layer

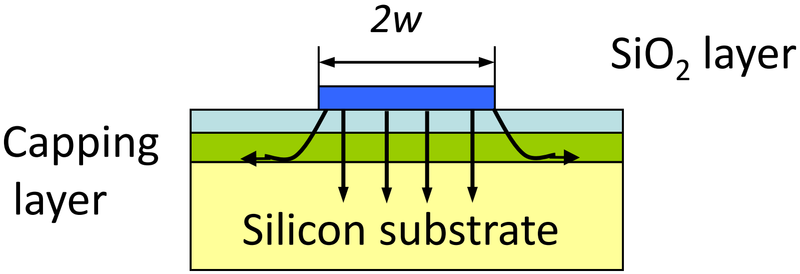
Thermal conductivity of Tin (Sn) Capping layer -- 3Ω Technique

- 99.999 % pure Sn (100 nm & 500 nm) sputtered on Si substrate at $2X10^{-7}$ Torr
- Insulating film – SiO_2 (PECVD using TEOS precursor at 150°C)
- Heater Lines – deposit Al using magnetron sputtering along with a microfabricated shadow mask



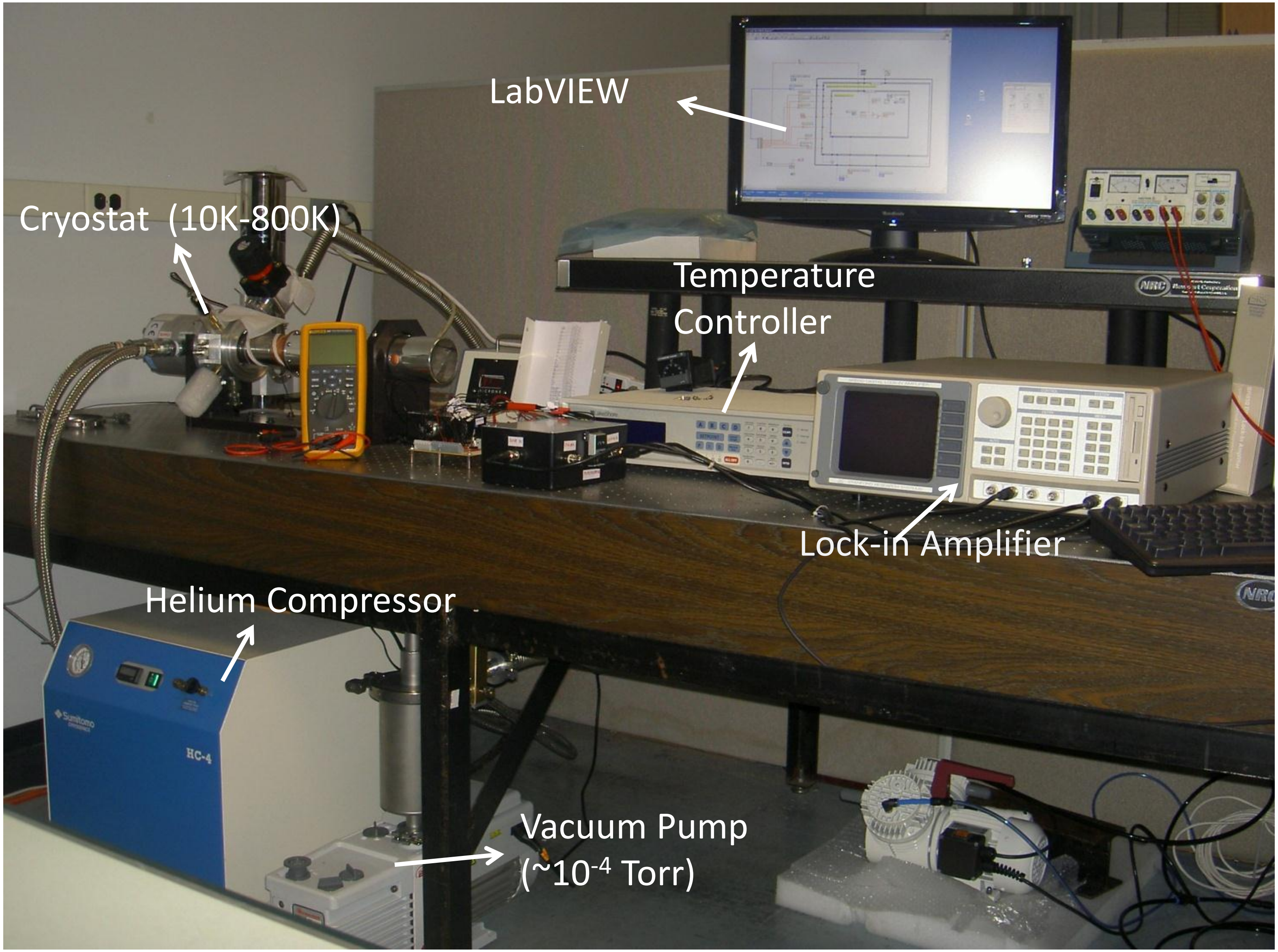


Pass current at I(ω)
Measure V(ω) & V(3ω)

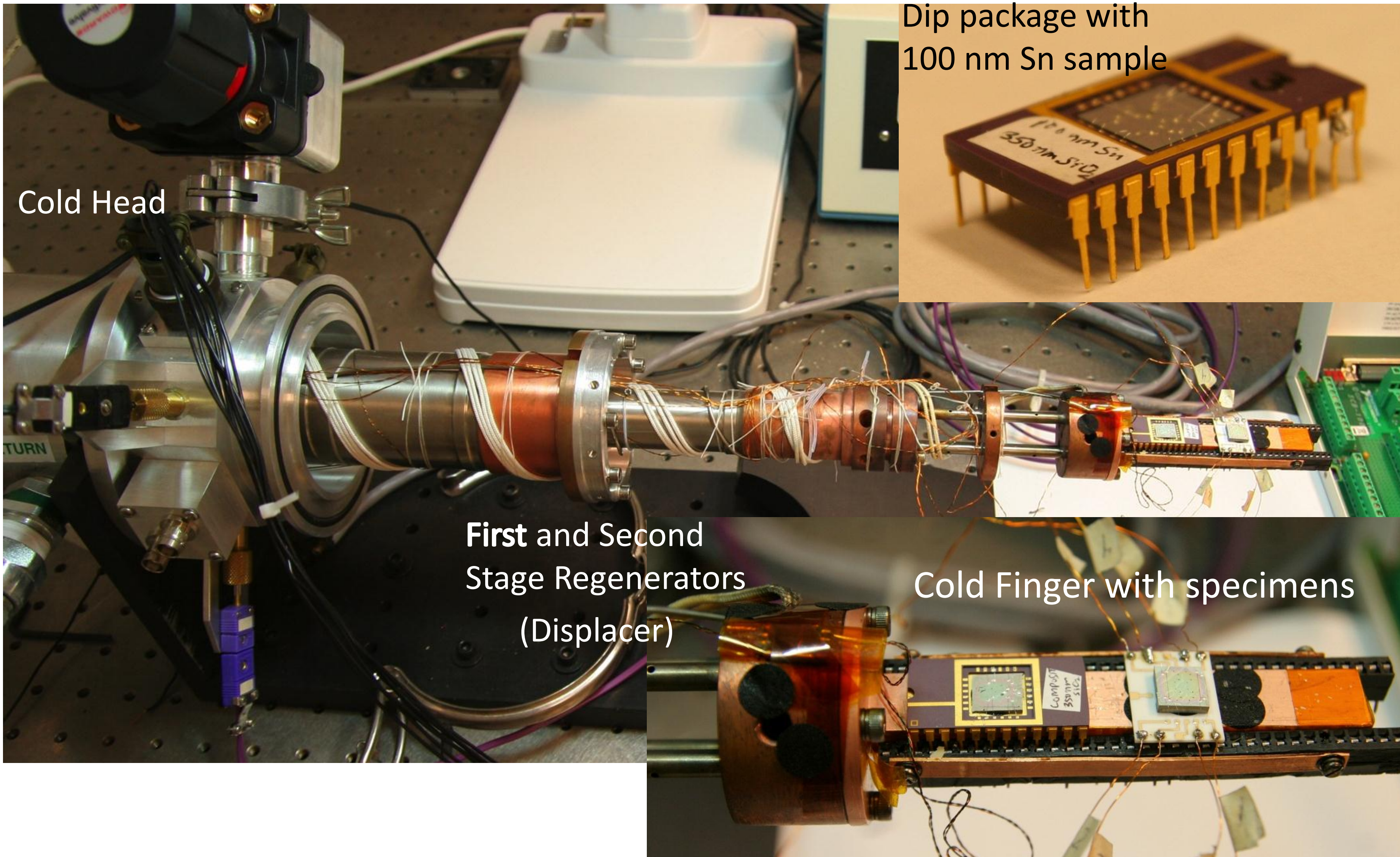


Thin Film Cross-Plane Thermal Conductivity

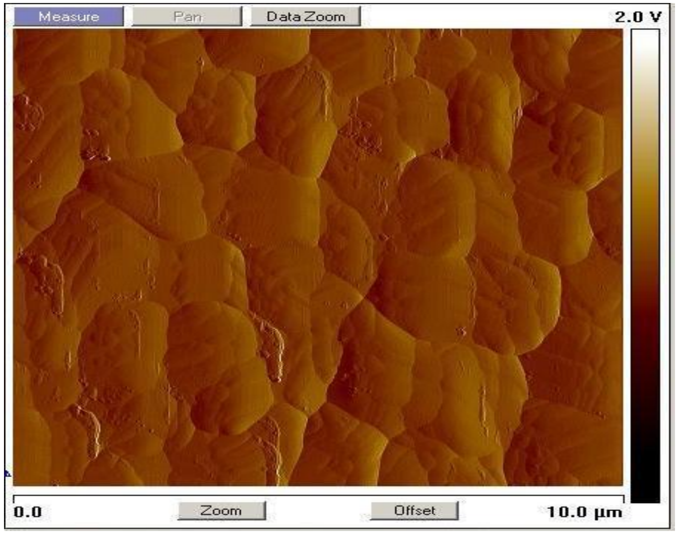
3Ω Experimental Setup

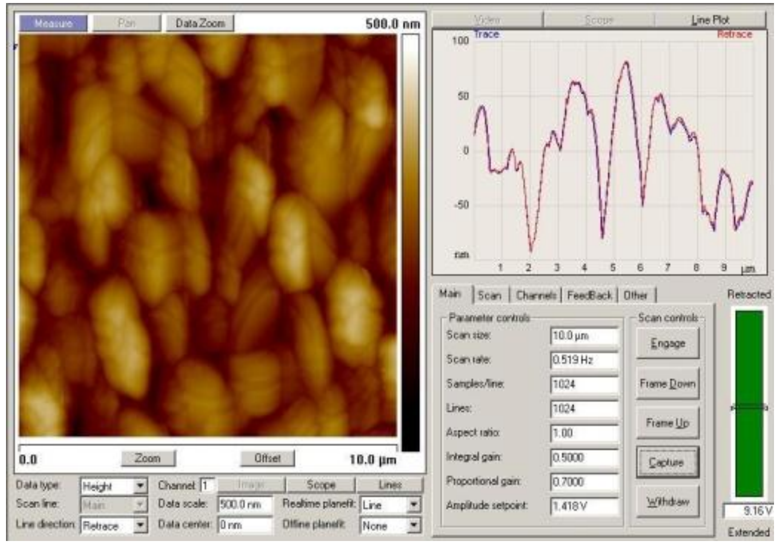


Cryostat with Specimen



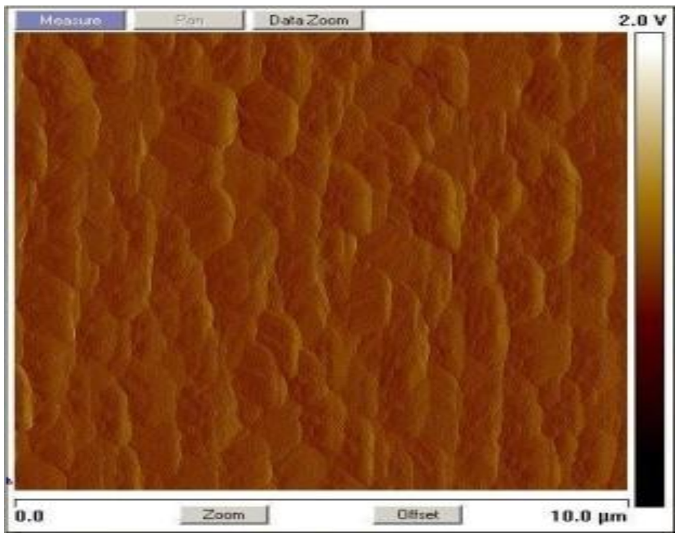
Sn Thin Film specimens (500 & 100 nm thick)

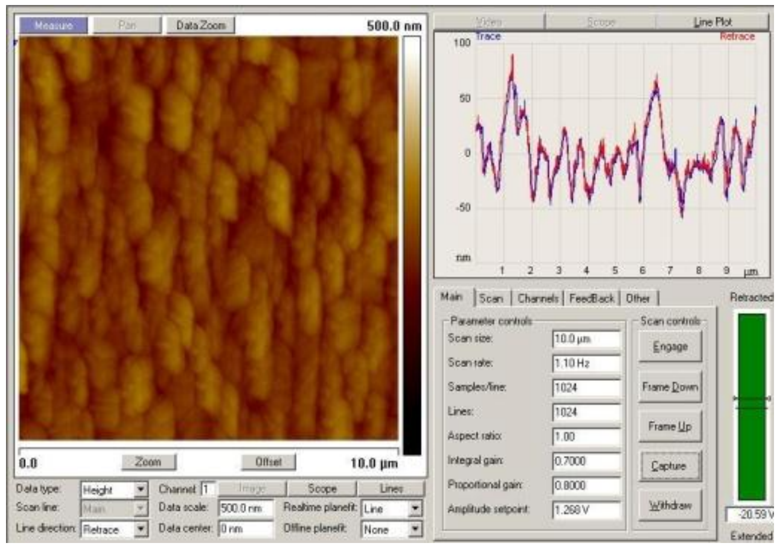




500 nm Sn film

Grain size:
450 to 2000 nm



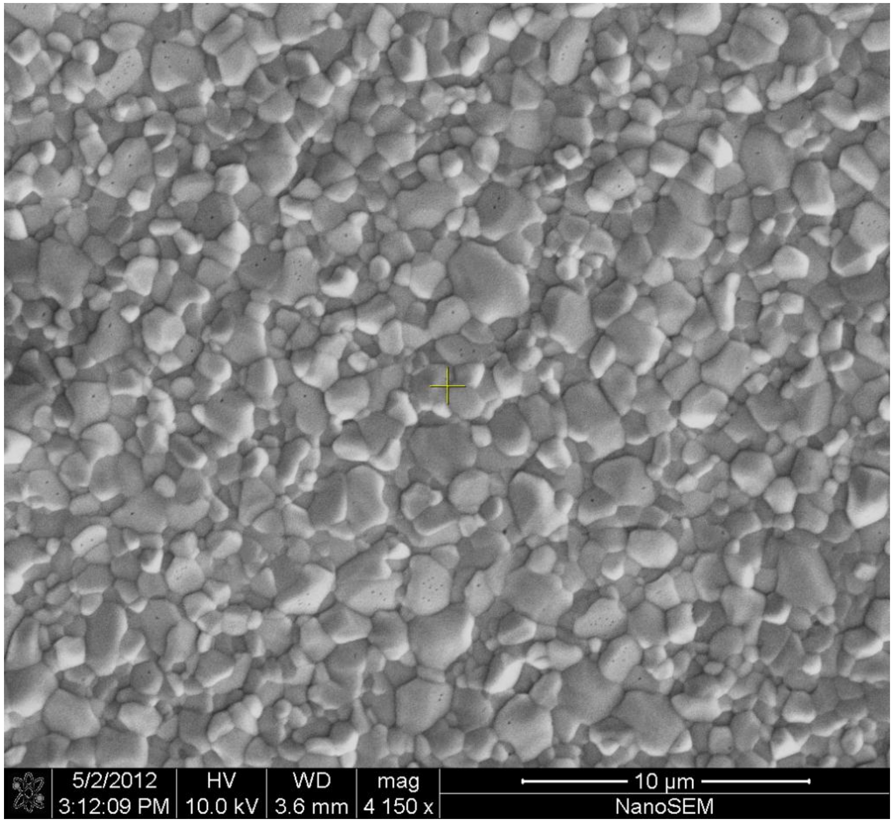


100 nm Sn film

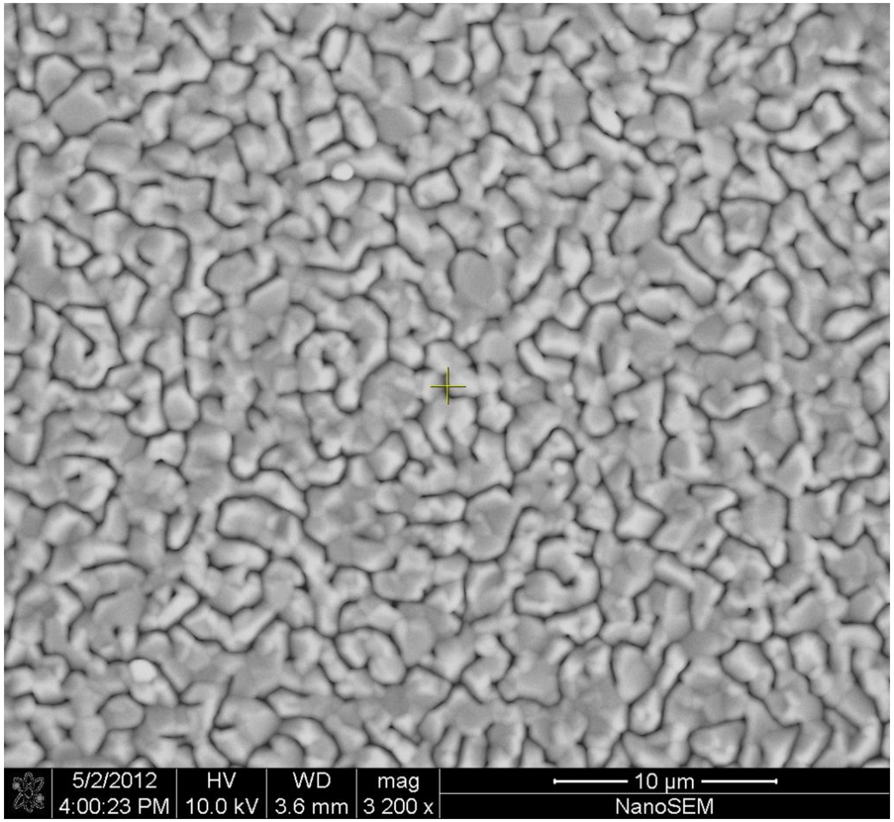
Grain size:
150 to 600 nm

Twin boundaries
within grains

SEM Micrographs



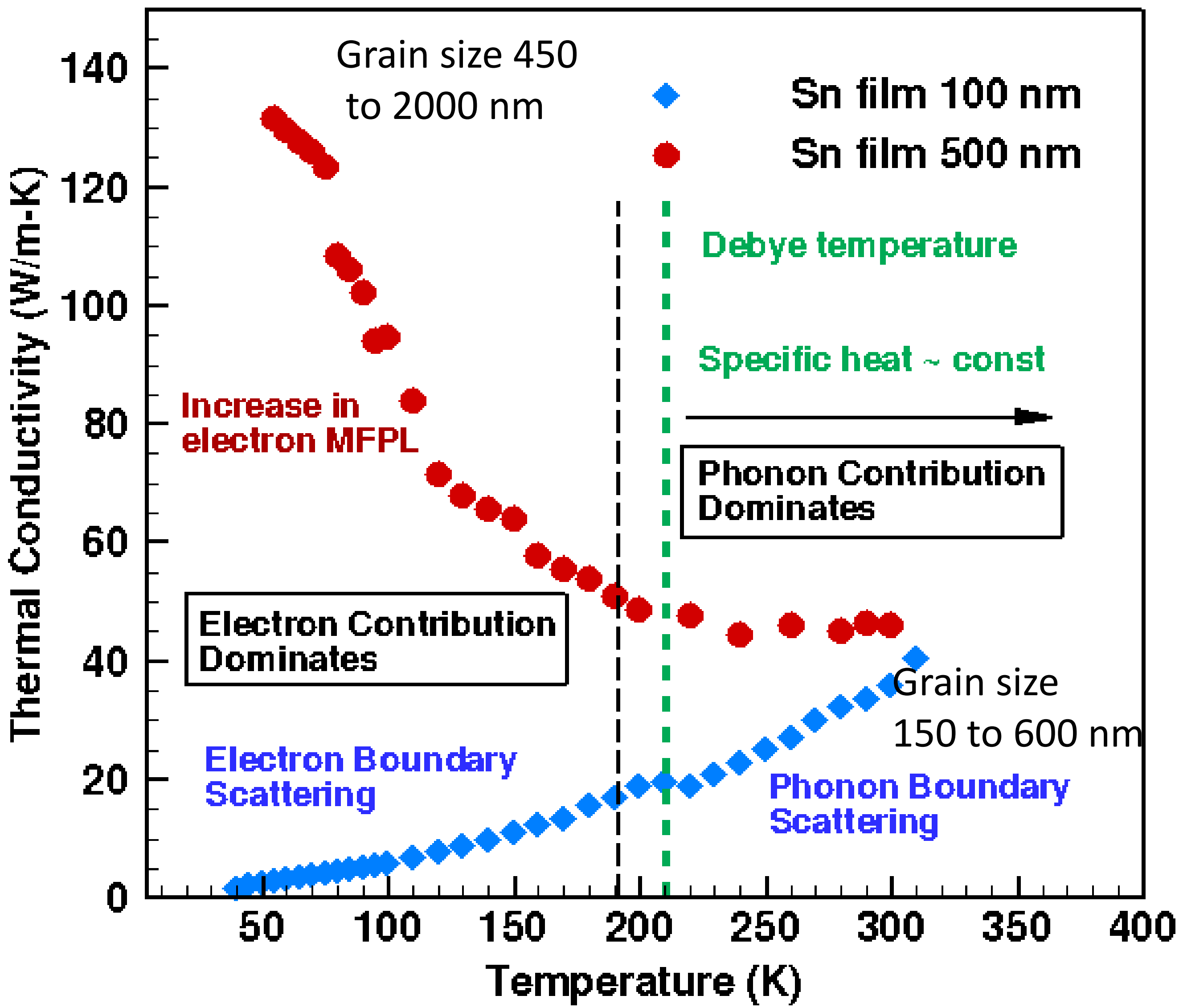
500 nm thickness



100 nm thickness

Thermal conductivity of Sn thin Films

(contribution from both electrons and phonons)



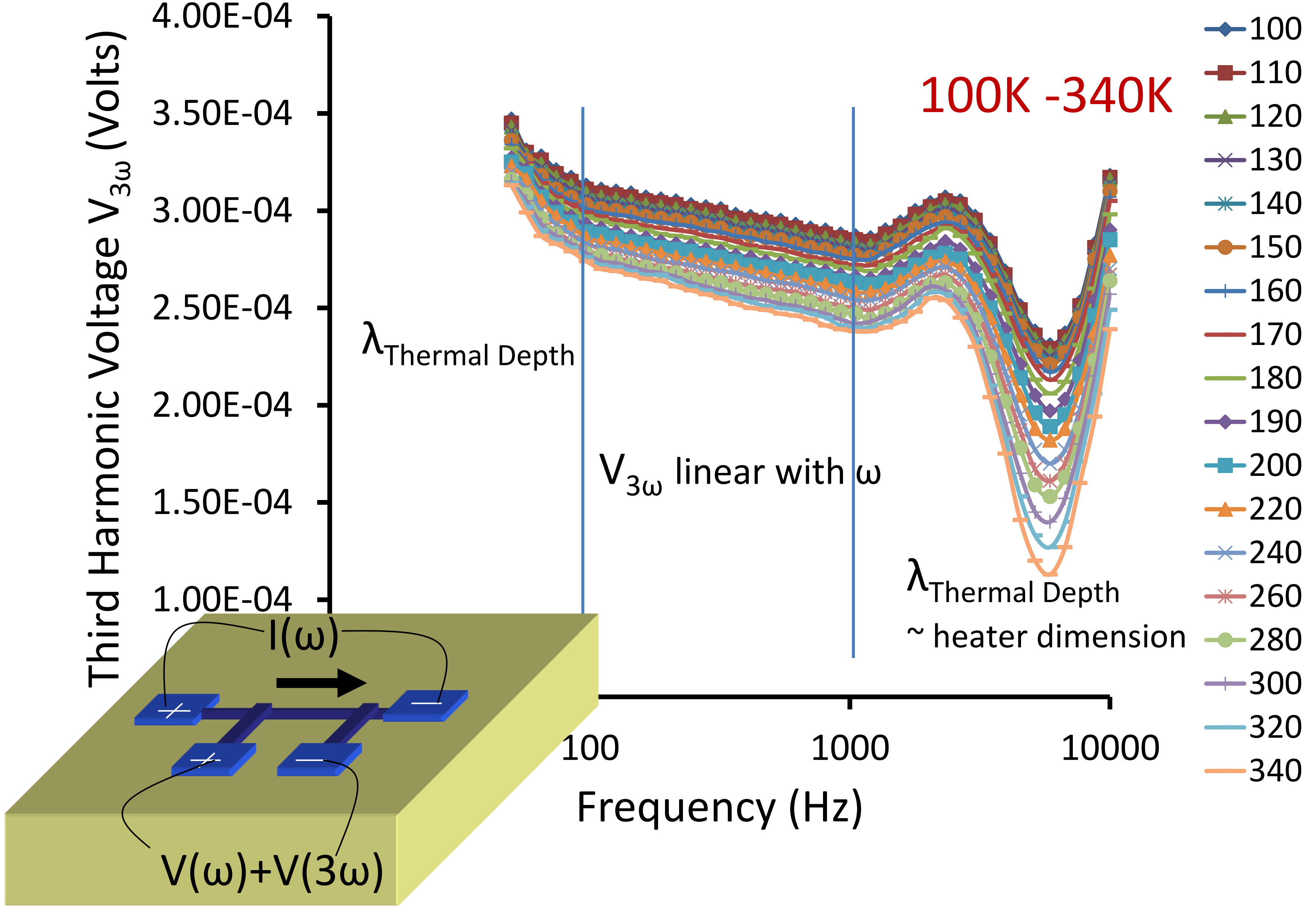
Phonon MFP
Room temp:
60 nm

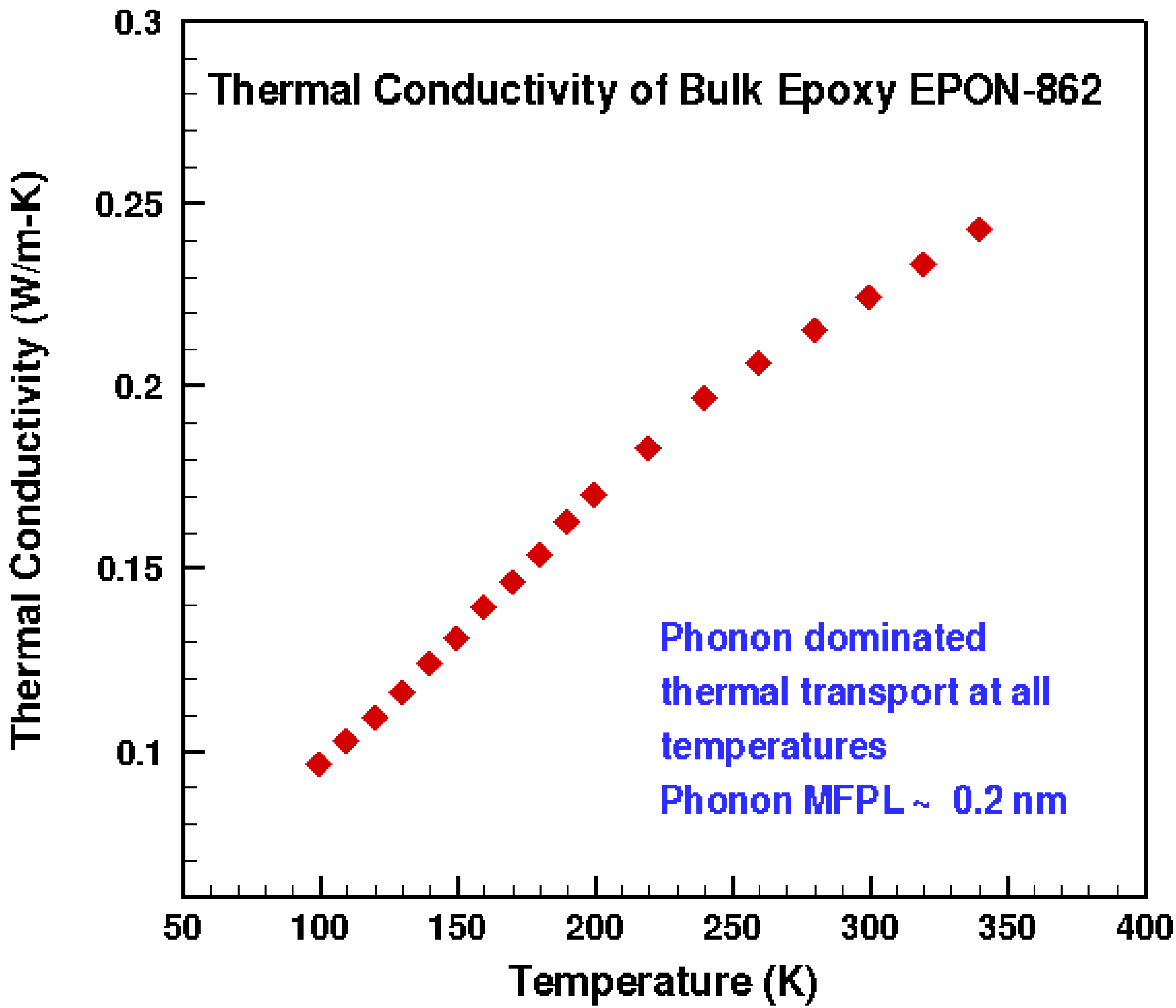
Electron MFP
(bulk)

Room temp:
2.8 nm

Low temp:
25 nm

Thermal Conductivity of Bulk Epoxy (Epon-862)





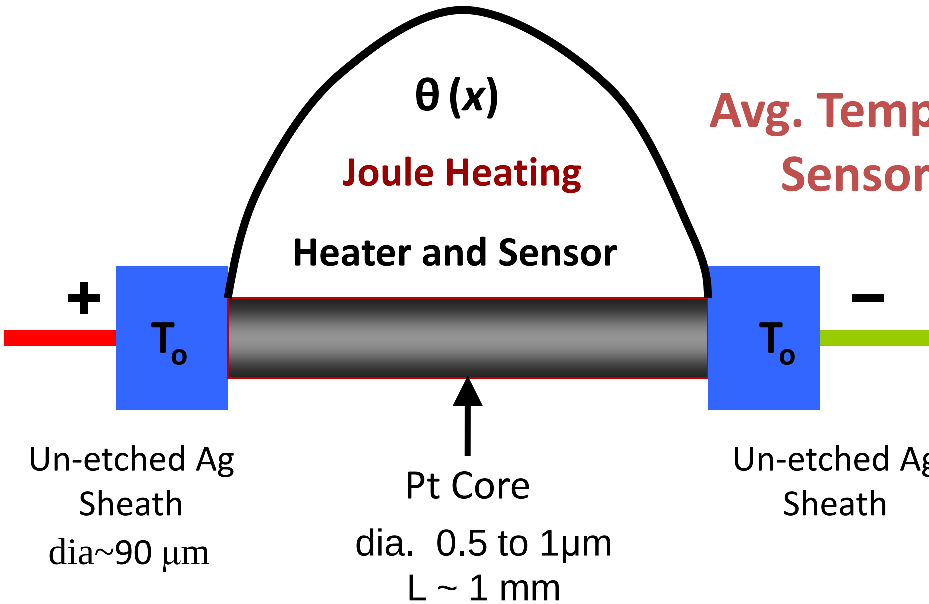
Thermal Conductivity of Bulk Epoxy EPON-862
Phonon dominated
thermal transport at all
temperatures
Phonon MFPL ~ 0.2 nm
Thermal Conductivity (W/m-K)
Temperature (K)
0.3
0.25
0.2
0.15
0.1
50
100
150
200
250
300
350
400

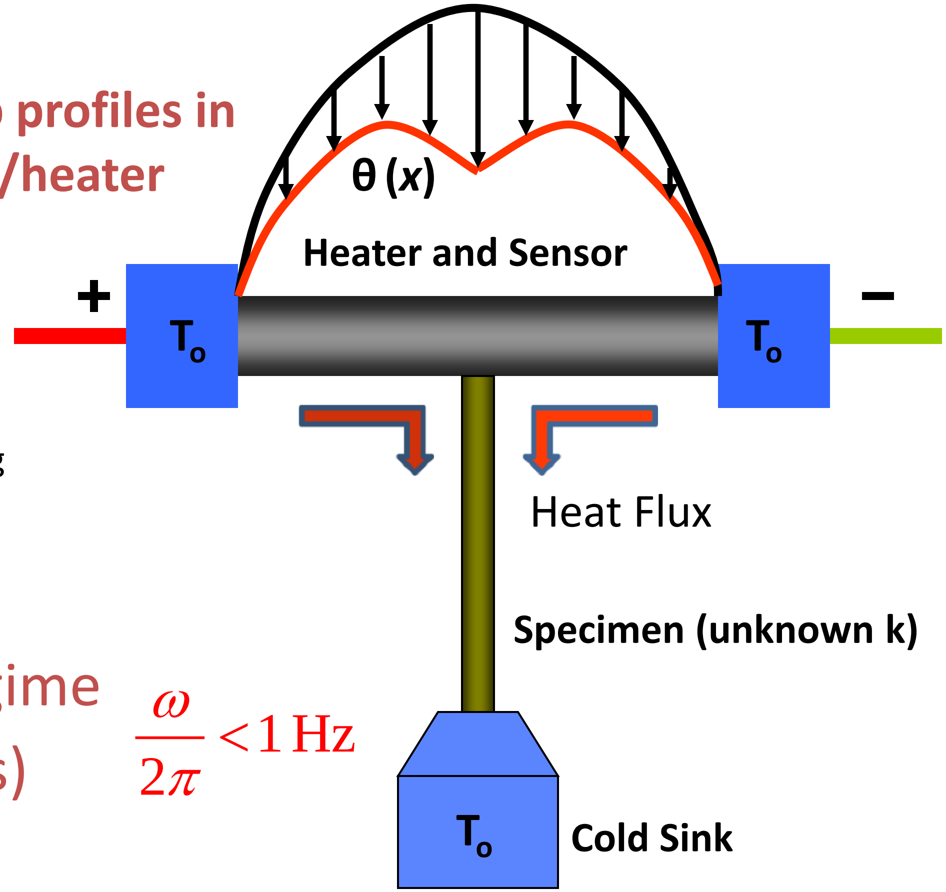
Thermal conductivity of Individual MWCNTs -- HOT WIRE PROBE

(Along with 3 Ω method)

Wollaston wire (Ag/Pt)-- heater and sensing probe

Sinusoidal current at ω leads to Joule heating in Pt. at 2ω; Voltage measurements at ω and 3ω





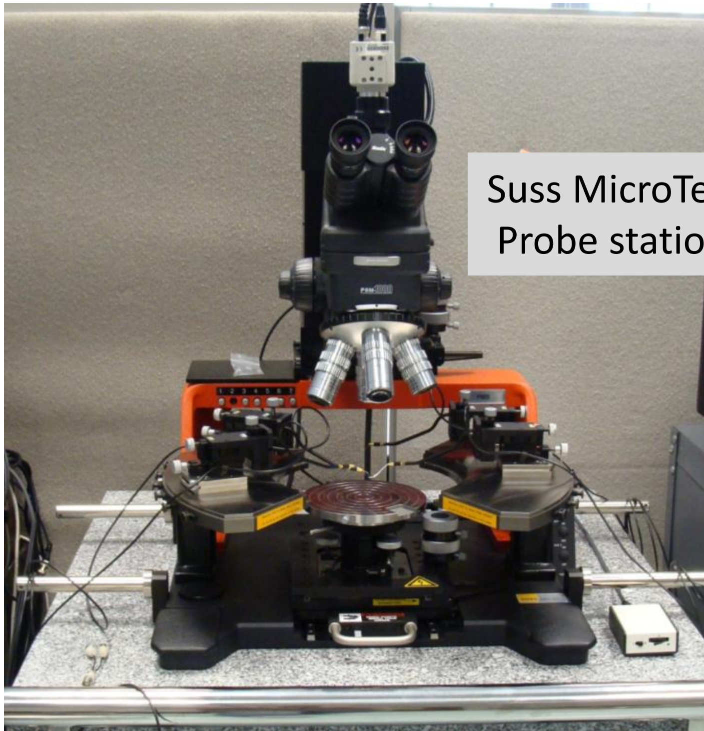
Low Frequency Heating Current Regime

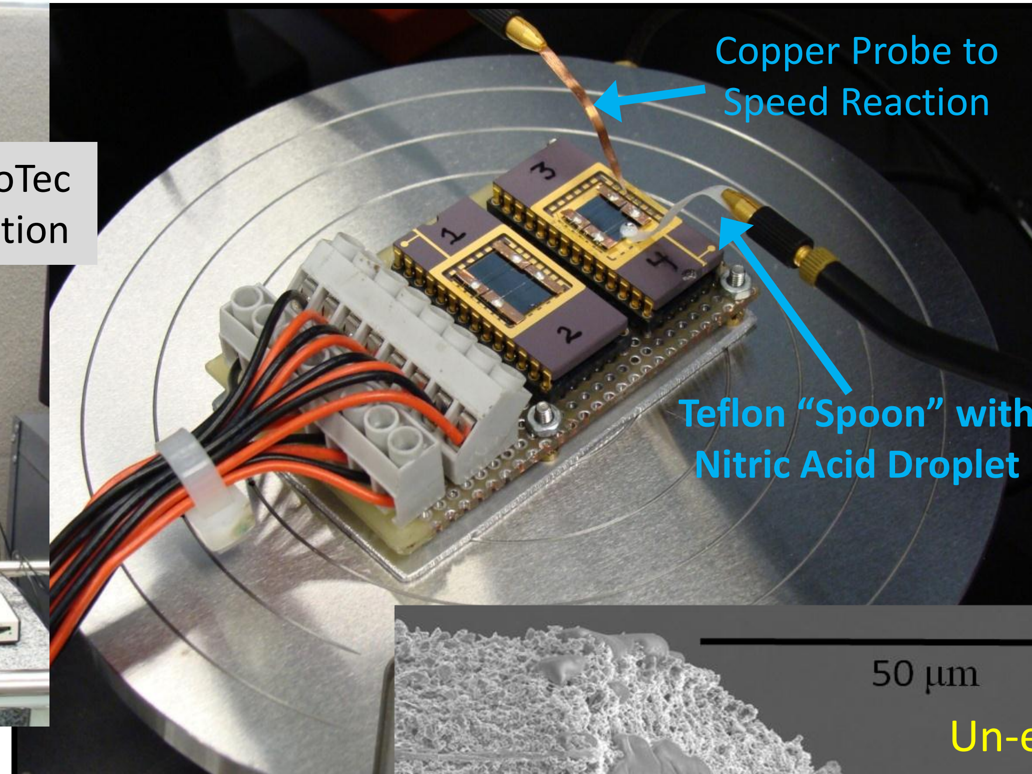
(Quasi steady-state thermal analysis)

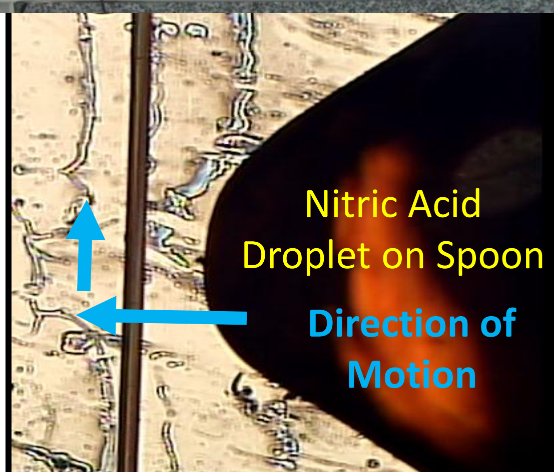
$$\frac{\omega}{2\pi} < 1\,\mathrm{Hz}$$

Change in average temperature -- Leads to a change in electrical resistance – leads to change in voltage at 3ω

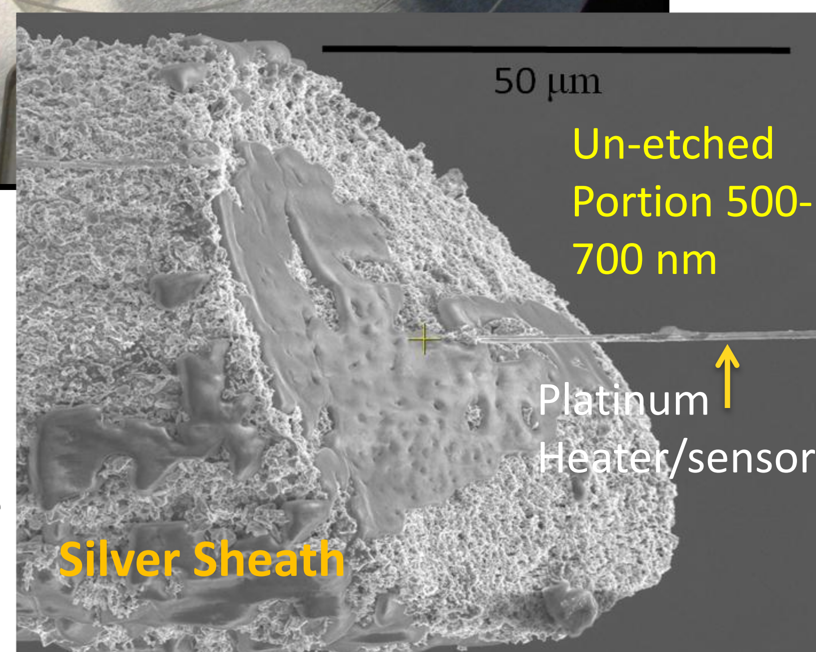
Etching the Wollaston Wire– Platinum sensor/heater wire

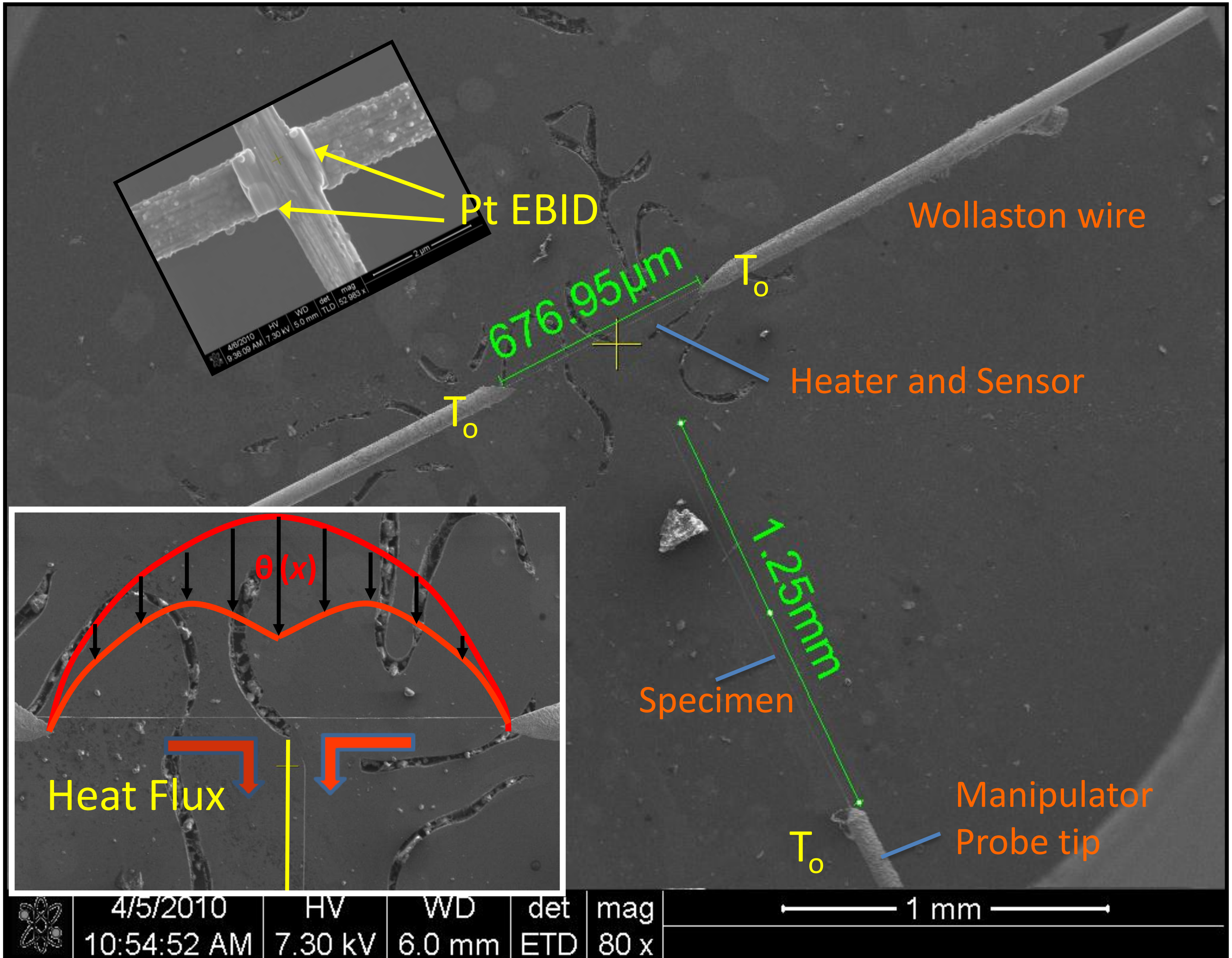






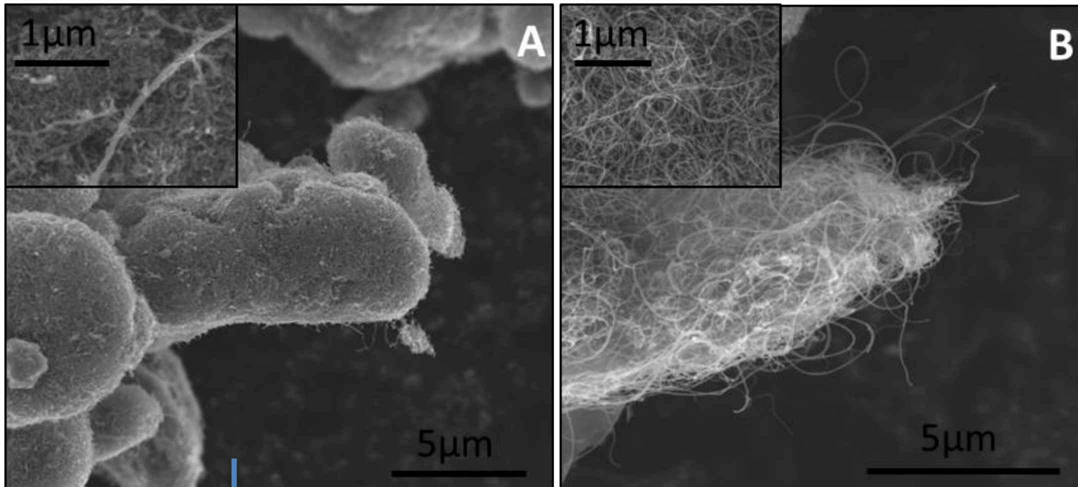
The copper and the teflon spoons are controlled using two micromanipulators in a Suss MicroTec Probe station





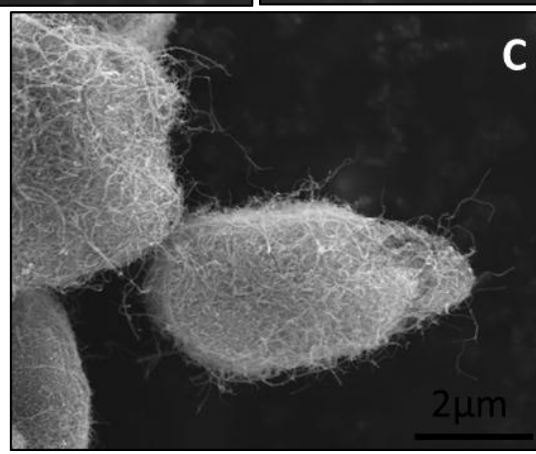
Pt EBID
Wollaston wire
676.95µm
T
o
Heater and Sensor
1.25mm
Specimen
Manipulator
Probe tip
θ (x)
Heat Flux
4/5/2010
10:54:52 AM
HV
7.30 kV
WD
6.0 mm
det
ETD
mag
80 x
1 mm

As-Received & Heat Treated (annealed) MWCNTs

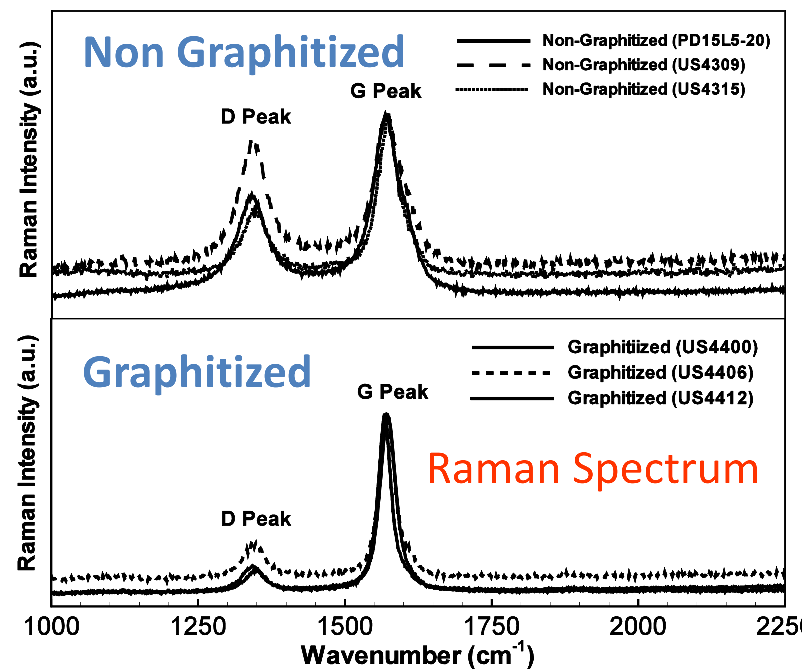


Non graphitized MWCNT
-- Nanolab Inc
-- US Nanomaterials Research

Graphitized MWCNT
- US Nanomaterials Research

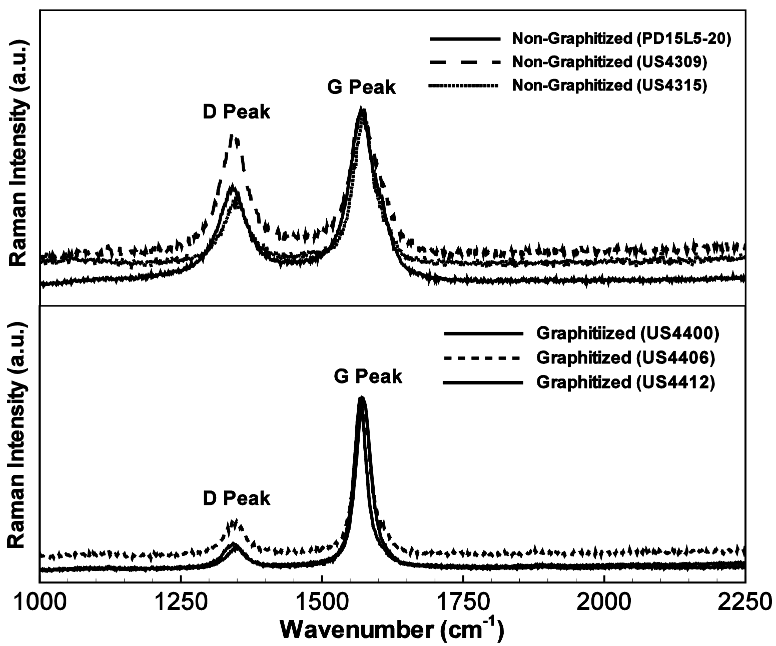


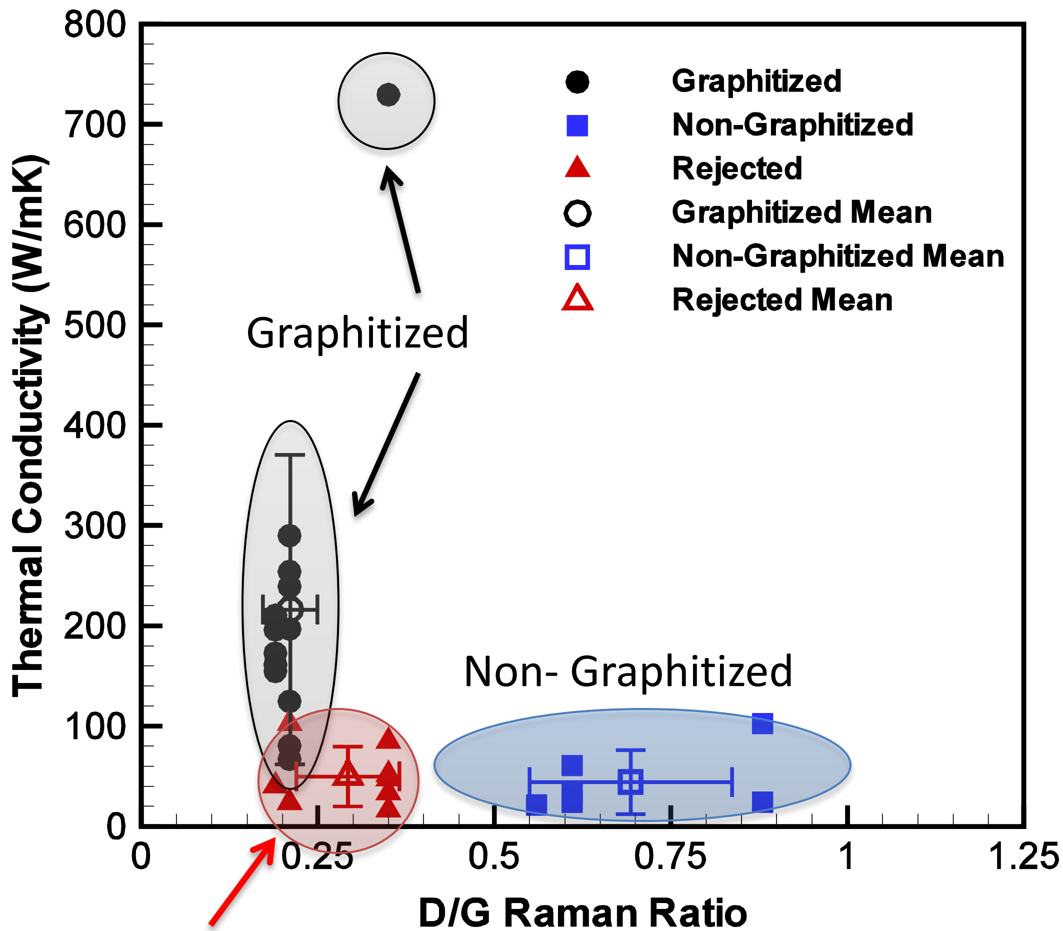
20 hour, 3000°C Post-annealing heat treatment



Smaller D/G ratio
Less number of defects

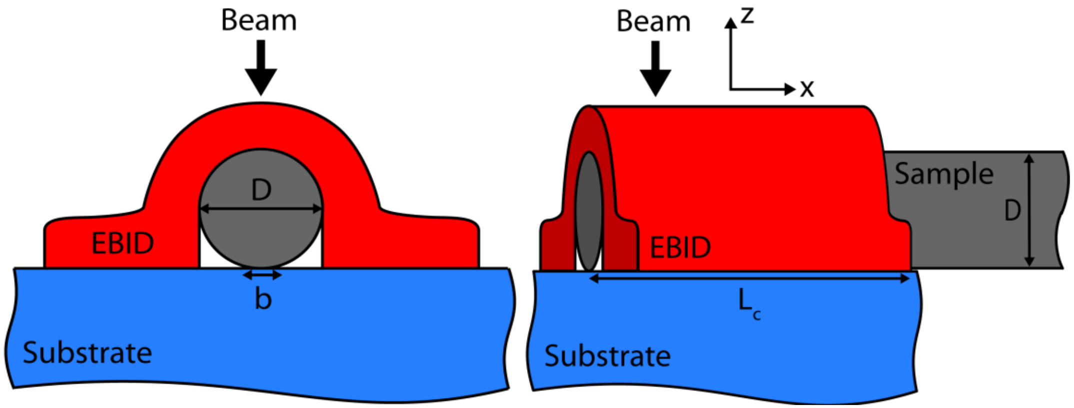
3Ω Measurements on Individual MWCNTs

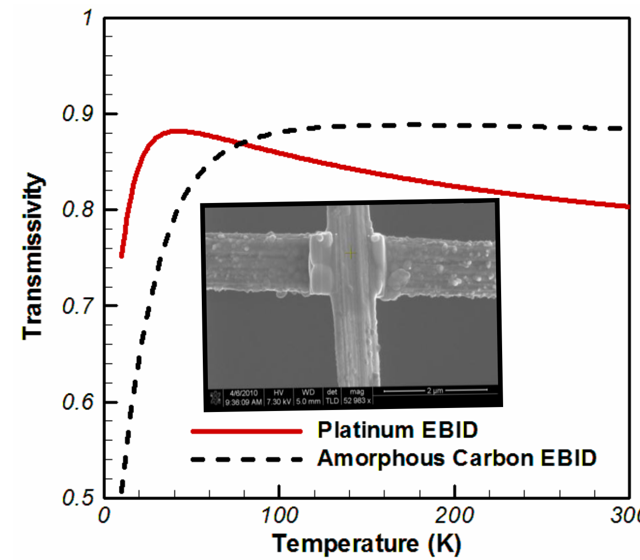




Graphitized but with morphological defects

Thermal Contact Resistance at the Pt wire-CNT Junction

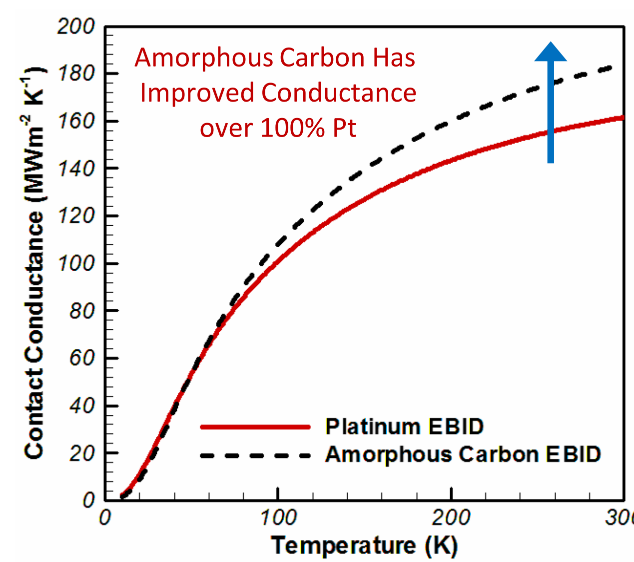




- **Required Information**
  - Phonon dispersion of EBID (Assume Debye Behavior since elastic properties have been measured[4])
  - Phonon dispersion of sample (Assume Graphite)
  - Contact width (*b*) estimated from elastic properties assuming van der waals forces of attraction
  - Contact dimensions *D*, L_c, are measured in SEM

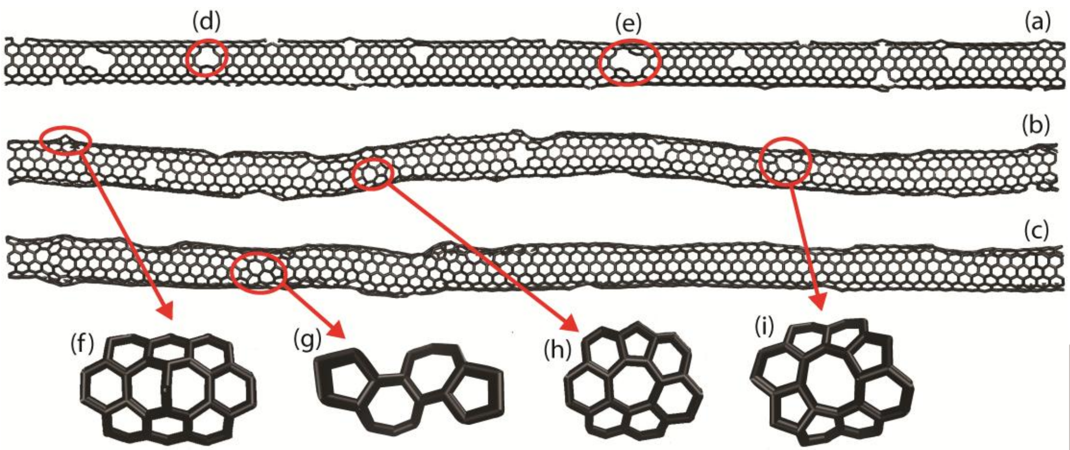
$$\alpha_{1-2} = \frac{\frac{1}{4}\sum_{3}\int_{\omega} n\hbar\omega v_2 DOS_2(\omega)d\omega}{\frac{1}{2}\frac{1}{(2\pi)^2}\sum_{\alpha}\int_{k_z}\int_{k_r} n\hbar\omega v_{1z}k_r dk_r dk_z + \frac{1}{4}\sum_{3}\int_{\omega} n\hbar\omega v_2 DOS_2(\omega)d\omega}$$

$$G_c = \frac{1}{R_c} = \frac{1}{2}\frac{1}{(2\pi)^2}\sum_{\alpha}\frac{d}{dT}\int_{k_z}\int_{k_r}\alpha_{1-2} n\hbar\omega v_{1z}k_r dk_r dk_z$$

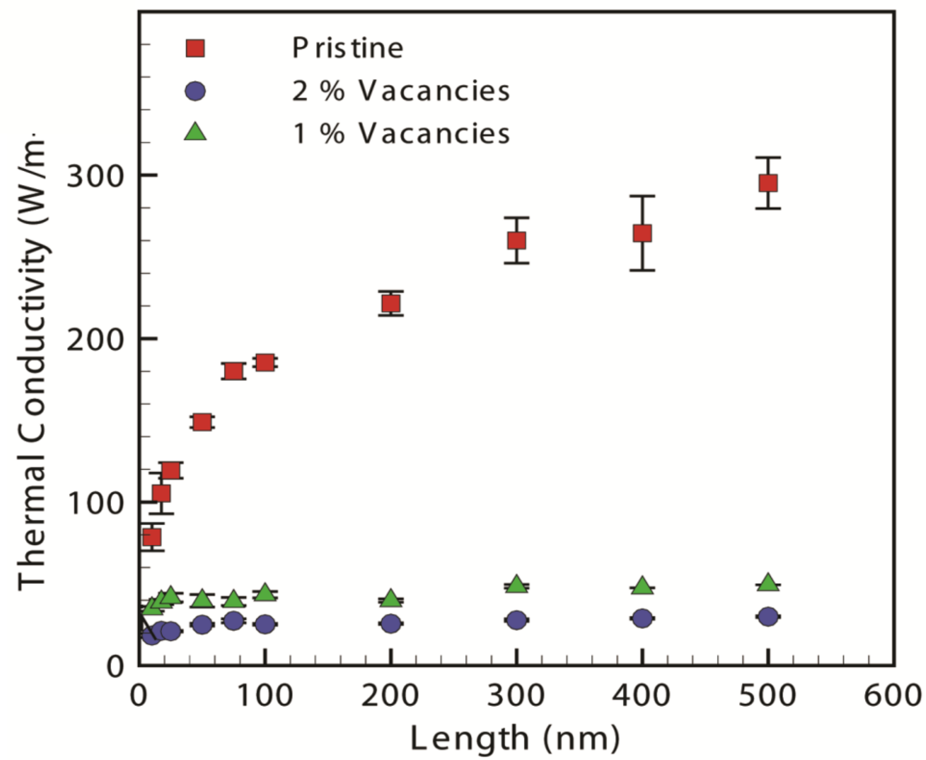


Correcting for contact conductance, k increases by 5% (Pt EBID)

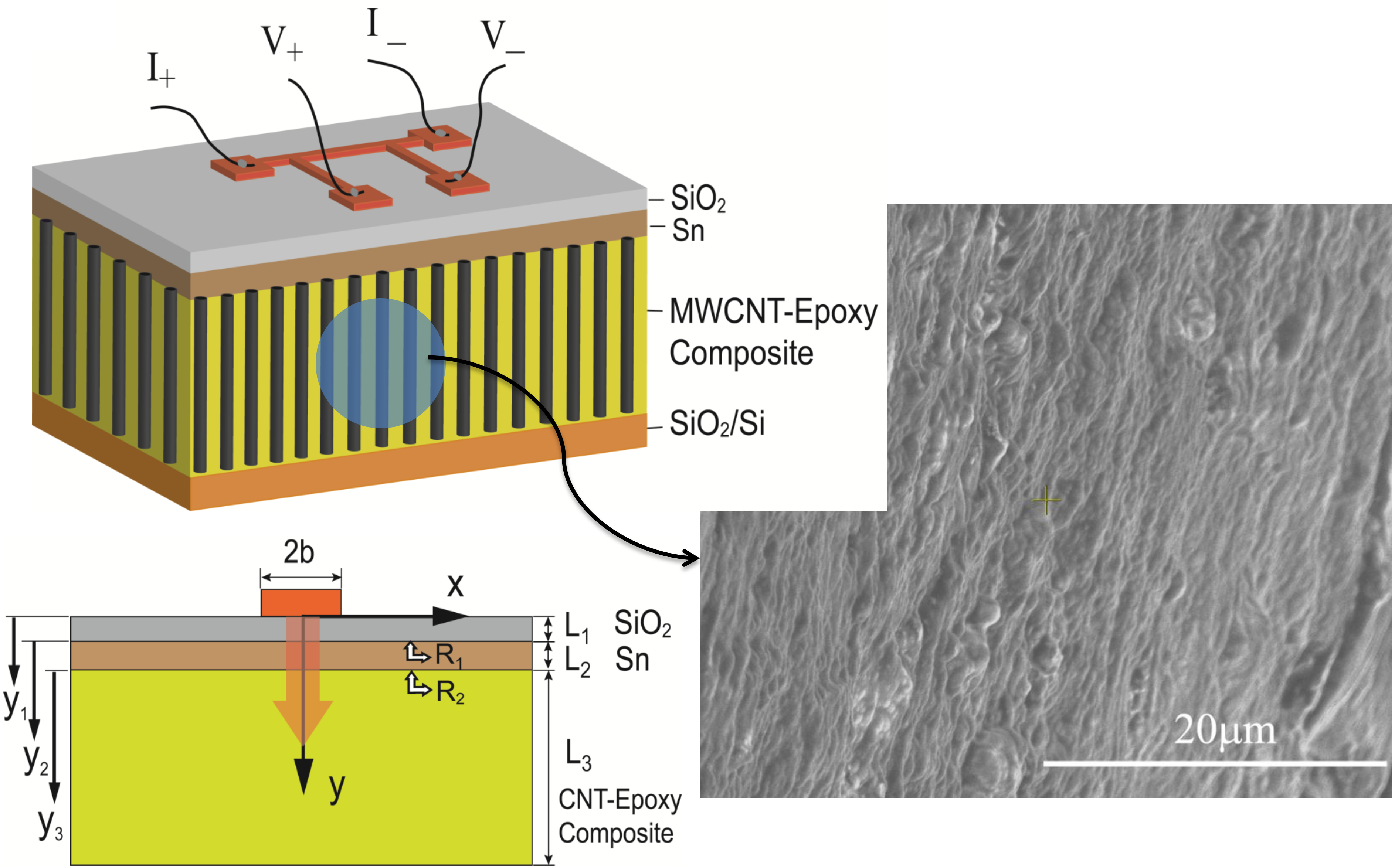
Molecular Dynamics: RNEMD



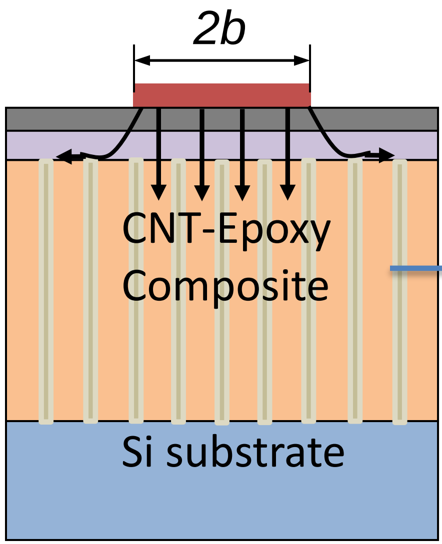
(6,6) armchair SWCNT
(with and without defects)



TIM Thermal Conductivity: 3Ω Method



TIM Thermal Conductivity: 3 Ω Experimental Results



Sample	Thickness	Thermal Conductivity @ RT	Thermal Resistance (L/k)
Oxide	350 nm	1.1 W/m-K	3.18×10^{-7} K/W
Tin	500 nm	46 W/m-K	1.08×10^{-8} K/W
CNT-Epoxy	2.1 mm	5.77 W/m-K	3.64×10^{-4} K/W

$$k_{system} = \frac{aV_{1w,rms}}{2p} \frac{Q_{avg}}{\ell} \frac{\ln(w_2 / w_1)}{V_{3w_1,rms} - V_{3w_2,rms}}$$

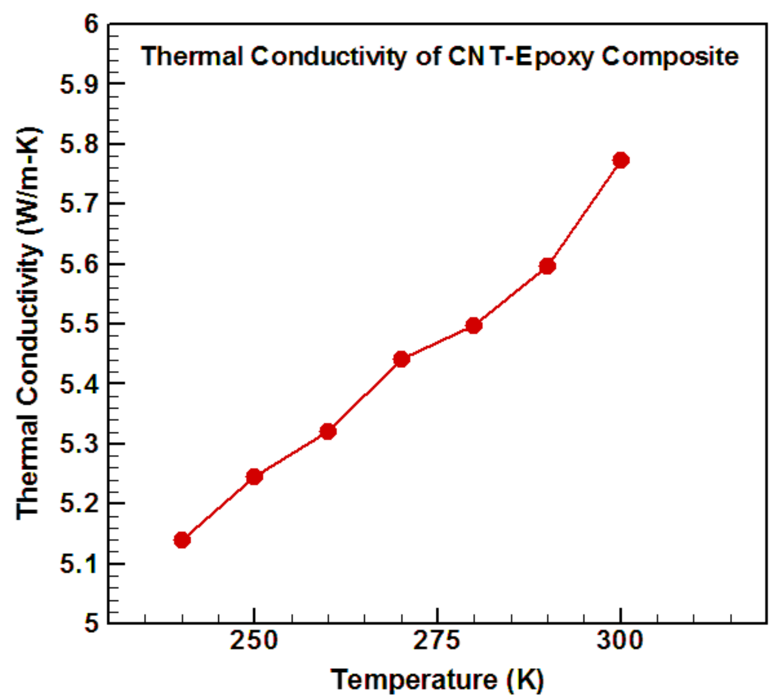
MWCNTs k ~ 60 W/m-K

- SiO_2 350 nm
- Sn 500 nm
- CNT-epoxy ~2.1 mm
- MWCNT 15-20 nm Dia
- Si 500 µm

1D Resistance Network

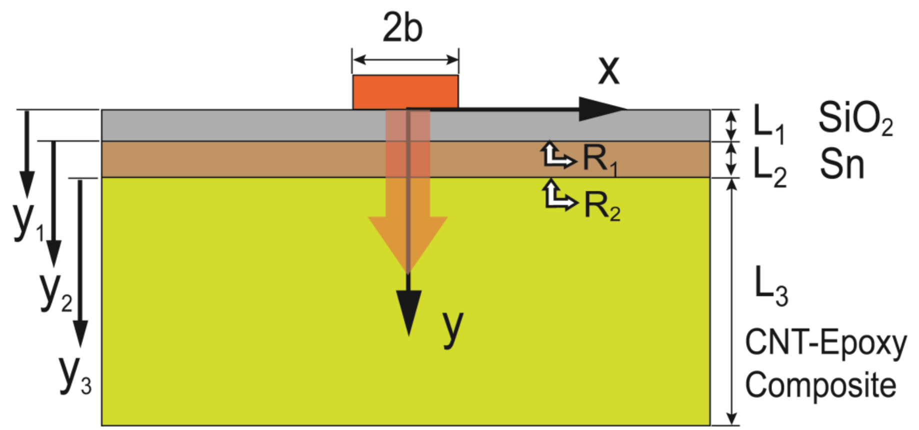
$R_{Eq} = \Delta T / Q$ $\quad R_{th_{Oxide}}$ $\quad R_{th_{Tin}}$ $\quad R_{th_{CNT-EpoxyComposite}}$

$$\frac{L_{System}}{k_{System}} = \frac{L_{Oxide}}{k_{Oxide}} + \frac{L_{Tin}}{k_{Tin}} + \frac{L_{CNT-Epoxy}}{k_{CNT-Epoxy}}$$



THERMAL MODEL (3 layer 1-D model)

$$T_j(y_j,t) = A.e^{(\eta_j y_j - i\omega t)} + B.e^{(-\eta_j y_j - i\omega t)}$$



$$\eta_j = \sqrt{-\frac{i\omega\rho_j C_{pj}}{k_{y,j}}}$$ (Inverse of the penetration depth)

$$q(y_1 = 0, t) = q_0 e^{-i\omega t}$$ (Heat Flux)

$$g_j = k_{y,j} h_j$$

Thermal Impedance

(without Interfacial resistance)

$$Z = \frac{T_1(0)}{q_o} = \frac{1}{\gamma_1}\left[\frac{\left(1+\frac{\gamma_3}{\gamma_2}\eta_2 L_2\right)+\left(\frac{\gamma_3}{\gamma_1}+\frac{\gamma_2}{\gamma_1}\eta_2 L_2\right)\eta_1 L_1}{\left(1+\frac{\gamma_3}{\gamma_2}\eta_2 L_2\right)\eta_1 L_1+\left(\frac{\gamma_3}{\gamma_1}+\frac{\gamma_2}{\gamma_1}\eta_2 L_2\right)}\right]$$

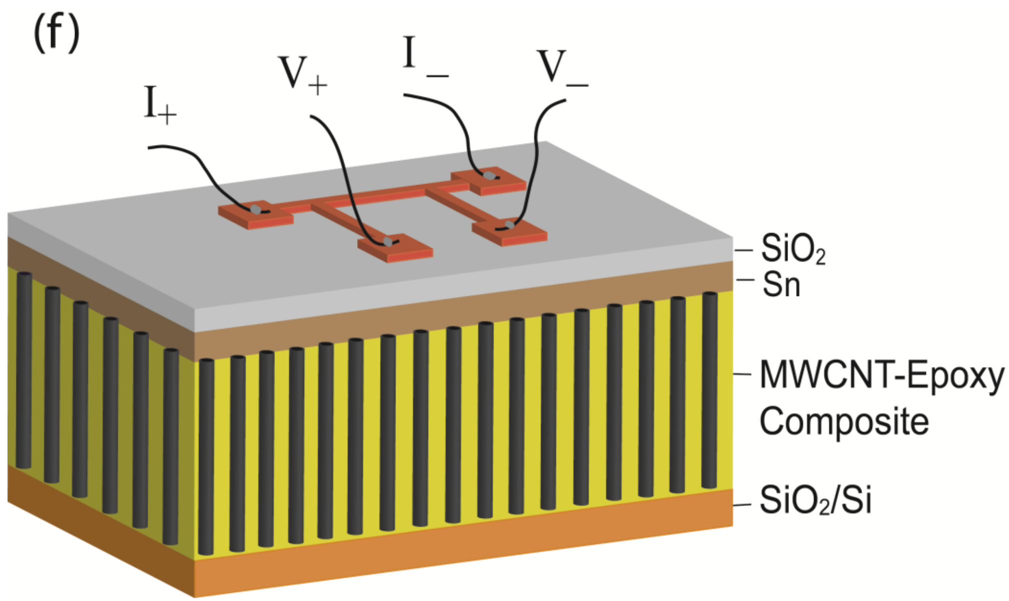
(with Interfacial resistance)

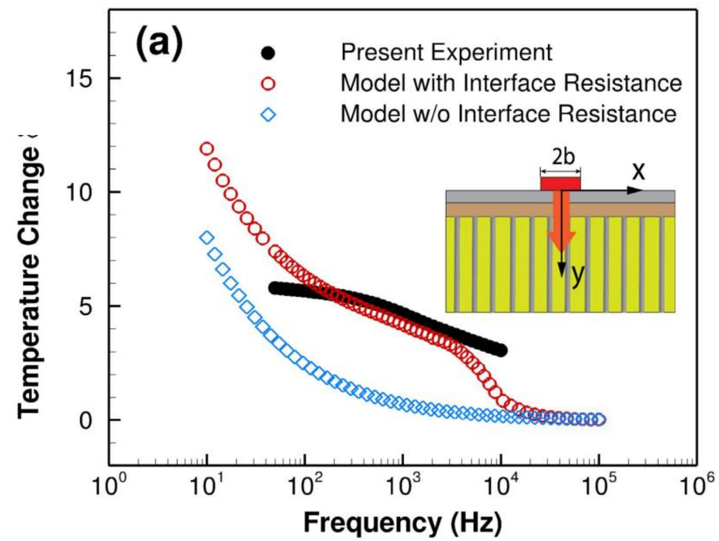
$$Z = \frac{1}{\gamma_1}\left[\frac{\left[(1+\gamma_3 R_1+\gamma_3 R_2)+\left(\gamma_2 R_1+\frac{\gamma_3}{\gamma_2}+\gamma_2\gamma_3 R_1 R_2\right)\eta_2 L_2\right]+\left[\frac{\gamma_3}{\gamma_1}+\left(\frac{\gamma_2}{\gamma_1}+\frac{\gamma_2\gamma_3}{\gamma_1}R_2\right)\eta_2 L_2\right]\eta_1 L_1}{\left[(1+\gamma_3 R_1+\gamma_3 R_2)+\left(\gamma_2 R_1+\frac{\gamma_3}{\gamma_2}+\gamma_2\gamma_3 R_1 R_2\right)\eta_2 L_2\right]\eta_1 L_1+\left[\frac{\gamma_3}{\gamma_1}+\left(\frac{\gamma_2}{\gamma_1}+\frac{\gamma_2\gamma_3}{\gamma_1}R_2\right)\eta_2 L_2\right]}\right]$$

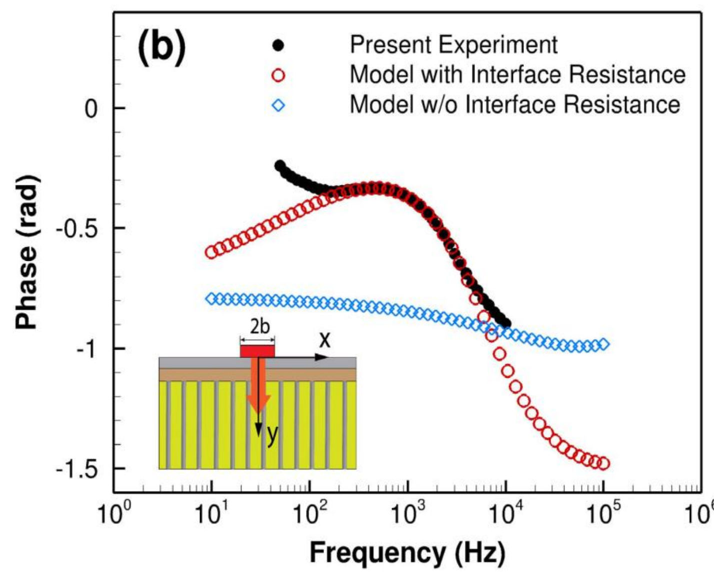
R_1 = *Thermal resistance* between SiO_2 and Sn

R_2 = *Thermal resistance* between Sn and MWCNT

Estimate Interfacial Thermal Resistance





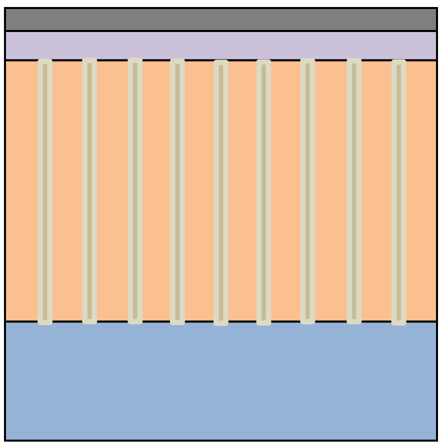


Thermal Interface Resistance between oxide and tin -- 5×10^{-5} m^2 K/W

Thermal Interface Resistance between tin and VA MWCNT -- 8×10^{-6} – 8.5×10^{-7} m^2 K/W

Estimate of Composite Thermal Conductivity based on the Rule of Mixtures

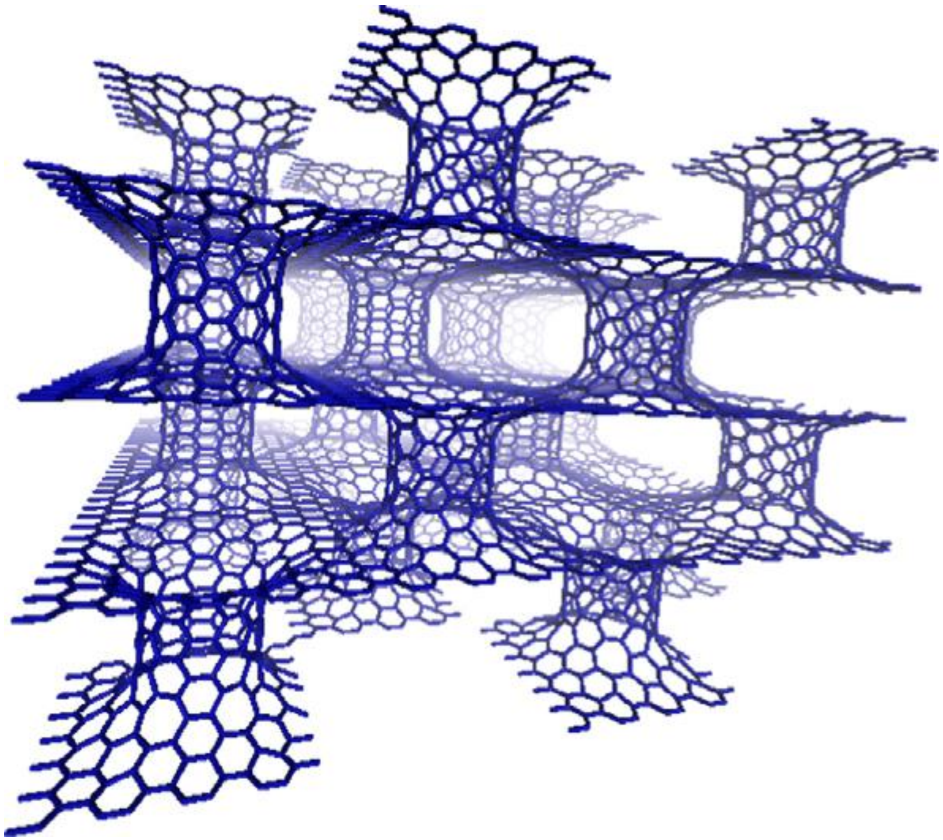
$$k_{Eff} = k_{Air} f_{Air} + k_{Epoxy} f_{Epoxy} + k_{CNT's} f_{CNT's}$$



Sample 10 X 11.5 X 2.1 (mm)	**Weight %**	**Density Kg /m^3**	**Volume %**	**Thermal Conductivity**
Carbon Nanotubes	12.91%	694	9.726%	**60 W/m-K** (*measured*)
Epoxy	86.97%	1090	41.764%	0.234 W/m-K (*measured*)
Air	0.11%	1.2	48.51%	0.026 W/m-K
CNT-Epoxy Composite				**5.77 W/m-K (Measured) 5.95W/m-K (predicted)**

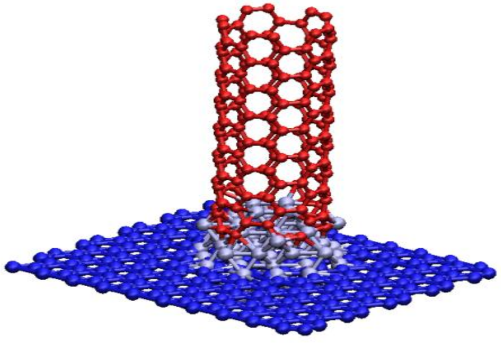
USE GRAPHITIZED VA MWCNT ARRAYS -- Can Push K_{TIM} ~ 20 W/(m-K)

3-D TIMS: Pillared Graphene-CNT Networks



- Inter-pillar distance
- Pillar length
- CNT-graphene nodes (junctions)

Provides avenues for both in-plane and cross-plane thermal conductivity



AFOSR MURI– 3D nanotube networks